Hydrogen abstraction from hydrocarbons: modeling of activation energies and pre-exponential factors

Maarten K. Sabbe, Aäron G. Vandeputte, Marie-Françoise Reyniers, Michel Waroquier, and Guy B. Marin
Laboratorium voor Chemische Technologie, Universiteit Gent, Krijgslaan 281
S5, B-9000 Gent, Belgium, +32 9 264 4516

Hydrogen abstraction reactions play an important role in many free-radical processes such as polymerization, combustion, pyrolysis and steam cracking of hydrocarbons. Accurate kinetic modeling of these complex processes requires a detailed reaction network that can contain hundreds of elementary hydrogen abstraction reactions. For every elementary reaction, kinetic parameters are required. The determination of all these kinetic parameters is one of the largest challenges in kinetic modeling. There are however only a limited number of experimentally determined kinetic parameters for hydrogen abstraction available in literature. And despite the increasing accuracy and computational performance, ab initio methods are still too demanding to determine accurate kinetic data for all hundreds of hydrogen abstractions in reaction networks, particularly for larger species. Therefore, parameterized methods such as group additivity based methods are often applied to predict the kinetics in large reaction networks.[1,2]

The group additive model described in this work allows the prediction of rate coefficients for bimolecular hydrogen abstraction reactions for a broad range of hydrocarbons in the temperature range 300-1300 K. This is an extension of the group additive model developed by Saeys,[3,4] which expresses activation energies with respect to a reference reaction, yielding the group additive values temperature-independent. Group additive values for 52 groups are derived from rate coefficients determined using the high level CBS-QB3 ab initio method, corrected for tunneling and the hindered internal rotation around the transitional bond. This ab initio computational approach yields a mean factor of deviation between experimental and calculated rate coefficients of 6 in the temperature range of 300-1000K.[5]

The presence of cross-resonance and hyperconjugative stabilization of the transition state is accounted for by introducing 4 corrections based on the transition state topology. The corrections, determined on a set of 28 reactions, are temperature-independent and reduce the mean absolute deviation to 0.7 kJ mol-1 on Ea and to 0.05 for logA. Final validation for 23 reactions yields a mean factor of deviation between group additive prediction and ab initio calculation of 3 at 300 K, and 1.6 at 1000 K. In a comparison with 6 experimental rate coefficients (600-719 K), the mean factor of deviation is less than 3.

References
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